



Competition between Silicifiers and Non-silicifiers in the Past and Present Ocean and Its Evolutionary Impacts

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Competition is a central part of the evolutionary process, and silicification is no exception: between biomineralized and non-biomineralized organisms, between siliceous and non-siliceous biomineralizing organisms, and between different silicifying groups. Here we discuss evolutionary competition at various scales, and how this has affected biogeochemical cycles of silicon, carbon, and other nutrients. Across geological time we examine how fossils, sediments, and isotopic geochemistry can provide evidence for the emergence and expansion of silica biomineralization in the ocean, and competition between silicifying organisms for silicic acid. Metagenomic data from marine environments can be used to illustrate evolutionary competition between groups of silicifying and non-silicifying marine organisms. Modern ecosystems also provide examples of arms races between silicifiers as predators and prey, and how silicification can be used to provide a competitive advantage for obtaining resources. Through studying the molecular biology of silicifying and non-silicifying species we can relate how they have responded to the competitive interactions that are observed, and how solutions have evolved through convergent evolutionary dynamics.

Keywords: diatoms, silicifiers, radiolarians, silicic acid transporters, silicification

INTRODUCTION

Biomineralization refers to the precipitation of minerals by living organisms (Simkiss and Wilbur, 1989). It may occur as a by-product of the normal metabolism of the organism under indirect genetic control—related to the cellular processes that create the conditions for incidental biomineral formation—and with no pre-concentration of specific mineral ions. Alternatively, the composition of the biominerals formed can be entirely dependent on the environmental conditions, for example, the formation of iron oxide by brown algae (Lee and Kugrens, 1989). By contrast, biologically controlled biomineralization requires direct genetic control, generates characteristically patterned structures, and involves selective uptake and pre-concentration of mineral ions.

In nature, we observe a wide array of biominerals (see **Figure 1**), ranging from iron oxide to strontium sulfate (Raven and Knoll, 2010), with calcareous biominerals being particularly notable (Knoll, 2003; Knoll and Kotrc, 2015). However, the most taxonomically widespread biomineral is silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), being present in all eukaryotic supergroups (Marron et al., 2016b). Notwithstanding, the degree of silicification can vary even between closely related taxa, from being found in composite structures with other biominerals (e.g., limpet teeth; Sone et al., 2007), to forming minor structures (e.g., ciliate granules; Foissner et al., 2009) or being a major structural constituent of the organism (Preisig, 1994). The most extreme degree of silicification is evident in the diatoms, where almost all species have an obligate requirement for silicon to complete cell wall formation and cell division (Darley and Volcani, 1969; Martin-Jézéquel et al., 2000). Biogeochemically and ecologically, diatoms are believed to be the most important silicifiers in modern marine ecosystems, with radiolarians (polycystine and phaeodarian rhizarians), silicoflagellates (dictyochophyte and chrysophyte stramenopiles), and sponges with prominent roles as well. In contrast, the major silicifiers in terrestrial ecosystems are the land plants (embryophytes), with other silicifying groups (e.g., testate amoebae) having a minor role.

Broadly, biomineralized structures are believed to have evolved and diversified where the energetic cost of biomineral production is less than the expense of producing an equivalent organic structure (Mann, 2001; Raven and Waite, 2004; Finkel and Kotrc, 2010). Raven (1983) calculated that the energetic costs of silicic acid uptake and silica structure formation is substantially more efficient than forming the same volume of an organic structure ($\sim 20\times$ more for lignin and $10\times$ for polysaccharides like cellulose). Based on the structural model of biogenic silica of Hecky et al. (1973), Lobel et al. (1996) identified by biochemical modeling a low-energy reaction pathway for nucleation and growth of silica. The combination of organic and inorganic components within biomineralized structures often results in enhanced properties compared to exclusively organic or inorganic materials. With respect to biogenic silica, this can result in the production of much stronger structures, such as siliceous diatom frustules having the highest strength per unit density of any known biological material (Hamm et al., 2003; Aitken et al., 2016), or sponge spicules being many times more flexible than an equivalent structure made of pure silica (Ehrlich et al., 2008; Shimizu et al., 2015). As a result, biogenic silica structures are utilized for support (Weaver et al., 2007), feeding (Nesbit and Roer, 2016), predation defense (Pondaven et al., 2007; Friedrichs et al., 2013; Hartley et al., 2016) and environmental protection as a component of cyst walls (Preisig, 1994). Biogenic silica also has useful optical properties for light transmission and modulation in organisms as diverse as plants (Schaller et al., 2013), diatoms (Fuhrmann et al., 2004; Yamanaka et al., 2008; Romann et al., 2015), sponges (Sundar et al., 2003), and molluscs (Dougherty et al., 2014). There is also evidence that silicification is used as a detoxification response in snails (Desouky et al., 2002) and plants (Neumann and zur Nieden, 2001), sequestering harmful substances such as aluminum and zinc within the biogenic silica to ensure the correct functioning of cellular metabolism. Diatom

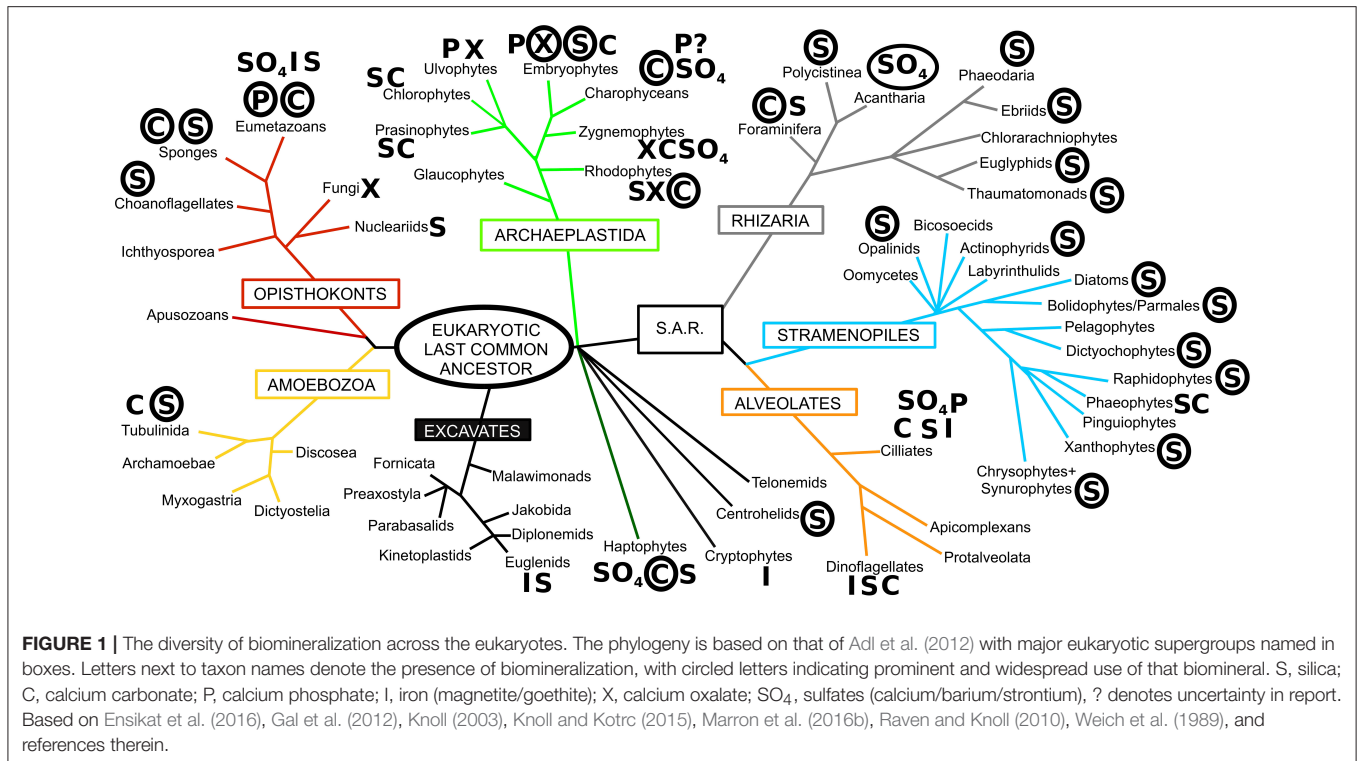
biosilica has even been suggested to play a role as a pH buffer for the enzymatic activity of carbonic anhydrase, aiding the acquisition of inorganic carbon for photosynthesis (Milligan and Morel, 2002).

The myriad of functions and benefits of biomineralization raises an important question: why do some organisms biomineralize while others do not? Furthermore, why is there such a diversity of biominerals besides silicon, when silicon is so abundant, comprising 28% of the Earth's crust? The answer to these questions lies in the evolutionary interplay between biomineralization and geochemistry, and in the competitive interactions that have arisen from these dynamics. Fundamentally whether an organism produces silica or not involves evolutionary trade-offs and competition between silicifiers themselves, and with non-silicifying organisms (both those which utilize other biominerals, and non-mineralizing groups). Mathematical models and controlled experiments of resource competition in phytoplankton have demonstrated the rise to dominance of different algal species based on nutrient backgrounds in defined media. These have been part of fundamental studies in ecology (Tilman, 1977; Sommer, 1994). However, the vast diversity of organisms that thrive in a complex array of biotic and abiotic interactions in oceanic ecosystems are a challenge to such minimal models and experimental designs, whose parameterization and possible combinations, respectively, limit the interpretations that can be built on them. Here we broadly extend our attention into other types of data from which competition can be inferred: the geological record, the distribution of species in modern marine ecosystems, and phenomena at the cellular and molecular levels (summarized in **Table 1**).

EVOLUTIONARY COMPETITION ACROSS GEOLOGICAL TIME

Competition between organisms is usually driven by a limited supply of a commonly used resource. For organisms that are biomineralizers of silica, orthosilicic acid—which we will refer to as silicic acid throughout, to distinguish from cellular silicon—is one such important limiting resource (Tilman et al., 1982). Silicic acid is released by the dissolution of biogenic silica and silicate minerals by biological and chemical weathering processes, and by hydrothermal activity, up to a solubility limit of 1.2–2.2 mM in water depending on the ambient physicochemical properties (Gunnarsson and Arnórsson, 2000). The drawdown of oceanic silicic acid through geological time has been attributed to biological utilization (Siever, 1991) and may have resulted in skeletal changes in marine silicifiers (Maldonado et al., 1999; Racki and Cordey, 2000; Lazarus et al., 2009; Finkel and Kotrc, 2010; Finkel et al., 2010; van Tol et al., 2012). To what extent these changes are a result of competition between silicifiers is still matter of debate.

The evolution of organisms that transport silicon into their cells has a long history (Marron et al., 2016b), likely going back to the evolution of cyanobacteria in the Archean (Dvůrák et al., 2014). As silicic acid is a small molecule, and is mostly



present in an undissociated form ($\text{Si}(\text{OH})_4$) under seawater pH conditions (Del Amo and Brzezinski, 1999), it is possible for silicic acid to diffuse across the cell membrane (Raven, 1983; Thamtrakoln and Hildebrand, 2008). In the high silicic acid Precambrian ocean, diffusion from the surrounding Si-saturated seawater could result in silica precipitating freely within the cytoplasm, interfering with cellular processes and disabling the functioning of the cell. Consequently, silicon transporters are proposed to have arisen initially to prevent intracellular toxicity by removing it from the cytoplasm (Marron et al., 2016b). Recently, cyanobacteria microfossils that contain nanocrystals of greenalite with the approximate composition of $\text{Si}_2\text{O}_5(\text{OH})_4\text{Fe}^{2+}$ (Lepot et al., 2017) have been found in the 1.88 Ga Gunflint Iron Formation, suggesting Fe biomineralization, which may also have protected oxygenic photosynthesizers against Fe^{2+} toxicity during the Paleoproterozoic.

It is inferred from the proliferation of biomineralized fossils in the geological record at the end of the Proterozoic and into the early Paleozoic that the ocean witnessed large reductions in silicic acid (Conley et al., 2017). The appearance of biomineralization (Kouchinsky et al., 2011; Knoll and Kotrc, 2015) likely led to evolutionary “arms races” with organisms using biomineralized structures to reduce predation rates, resulting in competition for an important shared resource (Smith and Szathmáry, 1995). This arms race produced a proliferation of non-silicic acid users and some highly efficient silicic acid users, the latter outcompeting inefficient users leading to their extinction.

There is widespread evidence in the geological record for such a decline in silicic acid and coincidental macroevolutionary changes in silicifying groups. For example, changes in chert

precipitation occurred due to the increased abundance of radiolarians in the lower to early Middle Ordovician, which may have reduced the abundance of sponges overall and forced the relocation of remaining sponge species from shallow to deep-water environments as surface waters became depleted in silicic acid (Kidder and Tomescu, 2016). In addition to the geological record, the timing of independent losses of silicon transporters (Marron et al., 2016b) further support the hypothesis that significant declines in silicic acid concentrations during the Paleozoic (Conley et al., 2017) led to evolutionary changes in the biochemical pathways of silicification and efficiency of silicon uptake.

However, it was the evolution of diatoms with their superior ability to utilize Si, due to their unique complement of Silicon Transporter (SIT) genes (Hildebrand et al., 1997, 1998), that led to the reduction of oceanic silicic acid concentrations to the low levels observed in the global ocean today (Tréguer and De La Rocha, 2013). Diatoms, with their obligate requirement for Si to complete their cell cycle, are strong competitors for silicic acid. This, combined with diatom features not related to Si (e.g., nutrient acquisition and storage, light harvesting, bloom formation), must have produced new competitive interactions that were previously unseen in the Paleozoic oceans (Knoll and Follows, 2016). Recent studies have robustly demonstrated the presence of very low oceanic silicic acid concentrations since at least 60 Ma, most likely as a result of the drawdown of silicic acid by diatom biomineralization (Fontorbe et al., 2016, 2017), which is tens of millions of years before the time period envisioned by Siever (1991) and others. Conley et al. (2017) have hypothesized that if such a global decrease in oceanic silicic acid concentrations

TABLE 1 | Examples of competitive interactions involving the use of silica, as seen from geology, ecology, and cellular/molecular biology.

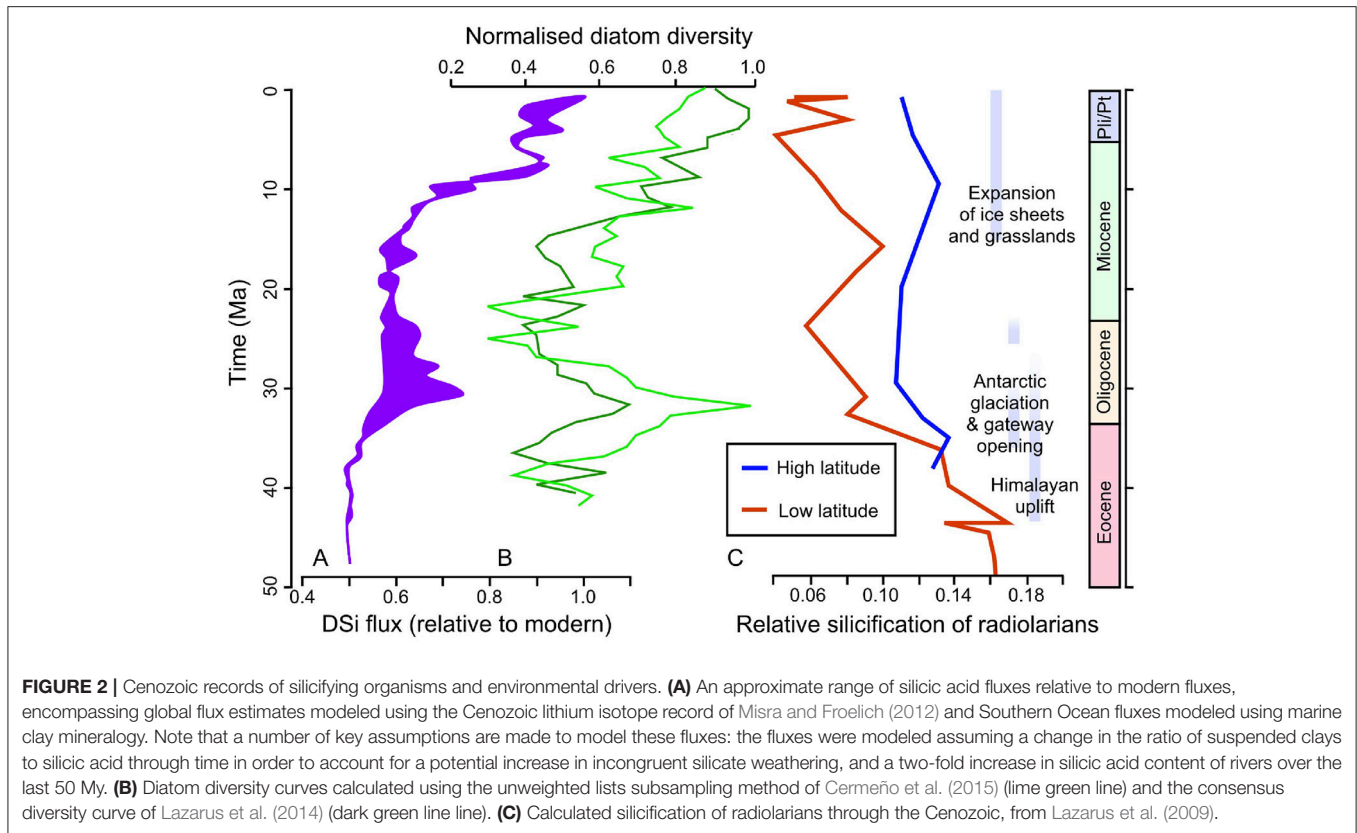
Level	Competitors	Description	Reference
Geological times	Radiolarians and sponges	Reduction of abundance and relocation of sponges in the early Middle Ordovician	Kidder and Tomescu, 2016
	Rise of diatoms: Diatoms and other silicifiers	Reduction of oceanic silicic acid in the Cenozoic (or even Mesozoic) era	Sims et al., 2006; Fontorbe et al., 2016, 2017
	Diatoms and sponges	Post-Mesozoic decline of certain sponge spicule morphologies	Maldonado et al., 1999
	Diatoms and radiolarians; Diatoms and silicoflagellates	Silicification and shell-thickness/spine morphology, decline of radiolarians in the low latitudes throughout the Cenozoic (reason still debated)	Lazarus et al., 2009; van Tol et al., 2012; Cermeño et al., 2015
Ecology in modern oceans	Diatoms and polycystines	Main users of silica	de Vargas et al., 2015
	Within silicifiers	Resistance against predators	Lebour, 1922; Marshall and Orr, 1955; Campbell et al., 2009; van Tol et al., 2012
	Silicifiers and others	Segregative pattern	Lima-Mendez et al., 2015
Cellular and molecular biology	Diatoms	Different morphologies that affect sinking, predation, light capture, viral resistance and nutrient uptake	Hamm et al., 2003; Fuhrmann et al., 2004; Raven and Waite, 2004; Losic et al., 2006; Sims et al., 2006; Pondaven et al., 2007; Yamanaka et al., 2008; Finkel and Kotrc, 2010; Nakov et al., 2014; Romann et al., 2015
	Diatoms and other silicifiers	Independent inventions of SITs in other silicifiers; SIT diversification in diatoms	Thamatrakoln et al., 2006; Durkin et al., 2016; Marron et al., 2016b
		Secondary loss of biosilicification in other silicifiers	Maldonado, 2009; Kozhemyako et al., 2010; Lahr et al., 2013, 2015; Zlatogursky, 2016
		Facultative biosilicification	Sandgren et al., 1996; Kessenich et al., 2014; Yamada et al., 2014; Leadbeater, 2015; Morueta-Holme et al., 2016

occurred, it must predate the Cenozoic and perhaps began with the appearance of silicifying diatoms in the Mesozoic (Sims et al., 2006).

Both the geological record and molecular phylogenetics concur that, whilst the majority of the main morphological groups of diatoms had arisen by the end of the Cretaceous (Kotrc and Knoll, 2015), there was a rapid expansion and diversification of diatoms in the Cenozoic (Siever, 1991; **Figure 2**). The most recent compilations have shown two short-lived major abundance peaks near the Eocene–Oligocene boundary and in the late Oligocene, with a shift in diatom abundance in sediments during the middle Miocene to globally higher values which have largely persisted to the modern day (Lazarus et al., 2014; Renaudie, 2016). There remains a lively debate in the scientific literature surrounding the drivers of the diatom expansion, mostly relating to shifts in the supply of silicic acid to the ocean due to changes in climate and weathering regimes. A correlation between a recent diatom diversity compilation and paleoclimate archives (oxygen and carbon isotopes from carbonates) indicates that there could be a direct link between temperature and diatom evolution throughout the Neogene (Lazarus et al., 2014). Climatically induced changes in oceanic circulation and mixing due to the opening of marine gateways may have altered nutrient availability in the euphotic zone and driven macroevolutionary shifts in the size of marine pelagic diatoms through the Cenozoic (Finkel et al., 2005). For example, geochemical archives point toward an increase in silicic acid supply to the surface Southern Ocean at the Eocene–Oligocene boundary, likely due to the

opening of the Drake Passage and Tasman Seaway and the formation of a “proto circum-Antarctic current,” and coinciding with the large peak in diatom diversification (Egan et al., 2013). The rapid rise of diatoms in the Cenozoic has also been attributed to the impact of orogeny on weathering (Misra and Froelich, 2012) with periods of enhanced continental weathering fluxes and increased silicic acid input to the oceans (Cermeño et al., 2015). Correlation between diatom abundance peaks and shifts in seawater strontium and osmium isotopic composition also hint at a strong control by silicate weathering on diatom deposition (Finkel et al., 2005). However, it is a major challenge to tease apart the impacts of oceanic circulation and weathering on diatom diversification and abundance due to the inherent coincidence in timing of the major orogenic episodes and shifts in oceanic circulation throughout the Cenozoic (Benoiston et al., 2017).

The expansion of diatoms, with their strong affinity for silicic acid, is likely to have led to competition with other silicifiers, especially in intermediate and shallow depths where silicic acid is present only in low—and potentially limiting—concentrations. Here the fossil record provides an archive for examining possible signs of competition in the geological past. The post-Mesozoic decline of certain sponge spicule morphologies, indicative of high silicic acid conditions in specimens from shallower waters, has been interpreted as showing competitive exclusion of sponges by diatoms (Maldonado et al., 1999). However, the exact timing of the decline in these spicules from shallower waters relative to diatom-driven changes in silicic acid is not well-constrained. If oceanic silicic acid declined earlier than the



Cretaceous-Paleogene boundary (Conley et al., 2017), then the exclusion of sponges from shallower waters either occurred due to competition at an earlier stage, or was driven by an alternative factor.

Changes in the size of radiolarians in the fossil record also provide evidence of macroevolution likely driven by competition. The silicification and shell-thickness of radiolarians in the low latitudes decline throughout the Cenozoic, whilst the higher latitude specimens remain invariant (Lazarus et al., 2009). This latitudinal pattern of change suggests that radiolarians increasingly struggled to obtain sufficient silicic acid in the lower latitude, oligotrophic waters, which were increasingly depleted of silicic acid due to a combination of diatom drawdown and shifts in oceanic circulation. However, despite the coincidence in timing, the decline in low-latitude radiolarian size does not necessarily point to competition as a driver of macroevolution. Mathematical models of competition between radiolarians and diatoms have been used to investigate this problem further. These experiments show that the reduction in radiolarian shell size is not sufficient to explain diatom diversification changes, which were more likely driven by an increase in resources and were linked inherently to their geographical distribution (Cermeño et al., 2015; **Figure 2**). However, these models are limited by the availability of reliable data on silicic acid inputs and fossil abundance records.

A combination of competitive interactions for silicic acid with other silicifiers and the effect of predator-prey arms

may govern macroevolutionary trends in silicoflagellate morphology (van Tol et al., 2012). Across the Cenozoic, silicoflagellate skeletons show two diverging trends: spineless species become smaller, whereas spiny species display decreased levels of silicification but increased numbers and length of spines. It has been interpreted that grazing pressure necessitated a siliceous skeleton for protection, as other phytoplankton (e.g., coccolithophores) also possessed biomineralized defenses. However, competition from diatoms reduced silicic acid availability and therefore increased the cost of producing such a skeleton. In response silicoflagellates may have evolved either to maintain the degree of silicification but became smaller overall, or to utilize spines as a method of retaining a large size and defensive structure but at a lower silicon requirement. These evolutionary trade-offs saw the extinction of large, spineless silicoflagellates as ecosystems changed through geological time to feature both high grazing pressure and low silicon availability.

One additional route for examining competition as a driver of silicifier macroevolution is the timing and extent of biochemical changes in silicon uptake pathways. The evolution of biochemical pathways for silicification have been investigated by resolving the different gene families that express, for example, silicon transporters in different silicifiers (Marron et al., 2016b). The affinity for silicic acid and the uptake efficiency of the different transporter families could then be assessed to determine the potential for competitive interaction between different silicifying groups, between and within major taxonomic groupings. Isotope

geochemistry could also be used as an additional tool for investigating this problem. Silicon transport into and within the cell is likely the basis for the fractionation of stable Si isotopes. All silicifiers investigated to date fractionate Si isotopes relative to the seawater in which they grow, but sponges have a more variable and potentially greater isotopic fractionation than either diatoms or radiolarians (de la Rocha et al., 1997; Hendry and Robinson, 2012; Hendry et al., 2014; Abelman et al., 2015). Such isotopic fractionation may be related to the biochemical pathways involved in Si metabolism, and may reflect the organism's affinity for silicic acid and efficiency of uptake and utilization. As such, Si isotopes may be a useful tool for examining the evolution of silicification.

EVOLUTIONARY COMPETITION IN MODERN ECOSYSTEMS

There are numerous examples of silicified structures being used by organisms to gain a competitive advantage in contemporary ecosystems. The siliceous lorica of choanoflagellates show a range of morphologies (Leadbeater et al., 2009), differing in size and density of siliceous components. This has been connected to niche partitioning, from large open structures that are required to maintain a planktonic lifestyle through the water column, to densely packed lorica of biofilm-inhabiting species (Leadbeater, 2015). The diatom *Phaeodactylum tricornutum* also displays evidence for optimizing its degree of silicification for deeper and colder waters (Zhao et al., 2014). Some wetland plants, notably rice, employ silica as a supplement to cellulose or lignin for structural strengthening, which allows taller growth and aids in competition for light (Cooke and Leishman, 2011).

The optical properties of silica can also be employed to aid in the absorption of light by photosynthetic organisms. Diatom frustules have been proposed to modulate solar wavelengths and direction for optimum absorption of light for photosynthesis (Yamanaka et al., 2008; Romann et al., 2015), while amorphous silica (in combination with microsporine-like amino acids) can help protect against harmful ultraviolet radiation (Ingalls et al., 2010). These adaptations can establish competitive interactions with other photosynthetic organisms that use different biominerals (e.g., calcium carbonate in coccolithophores Taylor et al., 2017, calcium oxalate in plants He et al., 2014), or organic components (e.g., flavonoids, Schaller et al., 2013) for similar photoprotective purposes.

Analysis of the distribution of silicifiers in the contemporary ocean at large spatial scale can bring additional insights about the evolution of competition between different groups. During the course of the *Tara* Oceans expedition (Karsenti et al., 2011; Bork et al., 2015), a worldwide characterization of pelagic plankton ecosystems was performed using DNA metabarcoding and microscopy correlated with key environmental parameters in a way that would, beyond acquisition of data, create a well-structured dataset to address broad ecological and evolutionary questions. Using a non-destructive *in situ* imaging system to visualize organisms directly in the water column (Underwater Vision Profiler, UVP), Biard et al. (2016) focused on the

abundance of giant Rhizaria in a variety of pelagic ecosystems in the upper 500 meters of the water column. Rhizaria is a supergroup of unicellular eukaryotes composed of three subphyla: Radiolaria, Cercozoa, and Foraminifera, some of which are silicified (Moreira et al., 2007; **Figure 1**). Radiolaria are divided into two major lineages: the siliceous skeleton producing Polycystinea (including the two orders Nassellaria and Spumellaria) and non-silicified Spasmalia (including Acantharia and Taxopodida; Krabberød et al., 2011). Phaeodaria, an asymbiotic rhizarian taxon with widespread biosilicification and extensively silicified lineages, was initially classified in Radiolaria and is now placed among the Cercozoa as revealed by molecular phylogeny (Polet et al., 2004). Phaeodaria was the most important contributor to rhizarian biomass at all latitudes in the 100–500 m depth layer, displaying an even distribution worldwide. On the contrary, photosymbiotic non-silicified Collodaria dominated the top 100 m of the water column at low latitudes, showing that these orders of Rhizaria display different ecological preferences and vertical stratification.

Additionally, the use of the 18S ribosomal DNA molecular marker to chart microbial diversity by metabarcoding (Taberlet et al., 2012) enabled a high-resolution taxonomic description of planktonic communities across several depths and various size fractions with reasonable accuracy (de Vargas et al., 2015), and was found to be a good proxy for cell number, at least within the diatoms (Malviya et al., 2016). Analysis of the *Tara* Oceans metabarcoding data revealed that diatom diversity was high in the open ocean, contrary to what was generally considered, and also confirmed diatom prevalence in regions of high productivity and at high latitudes. Ocean circulation choke points such as Cape Agulhas and the Drake Passage were found to be important in constraining diatom distribution and diversity (Malviya et al., 2016).

Beyond individual studies of major silicifying groups, comparative analysis can be performed using the *Tara* Oceans data set (de Vargas et al., 2015). Functional annotation of the silicifying organisms (based on Marron et al., 2016b), followed by mapping of their distribution across the global ocean, reveals major patterns (**Figure 3**). The silicifier community is largely size-delineated: the smallest size fraction (0.8–5 micron) contains a large diversity of silicifying organisms in nearly constant proportions. Dictyochophyceae, Polycystinea, and Chrysophyceae are the major taxonomic groups present in this size fraction, together with Bacillariophyta (diatoms) at some locations. Although less abundant, the constant presence of Centrohelida and Choanoflagellates suggests that ecological niche enables the coexistence of several taxonomic groups.

A larger size fraction of micro-plankton (20–180 microns) displays a very different trend. Diversity within the silicifier community drops, and is composed essentially of only Bacillariophyta and Polycystinea, so much so that both taxonomic groups represent over 99% percent of the micro-planktonic silicifier community across the vast majority of the global ocean. Diatoms and polycystines occur in highly variable proportions, where diatoms dominate the cold high-latitude regions. Co-existence between both groups is rare, whereby the presence of one of the organisms appears to exclude the

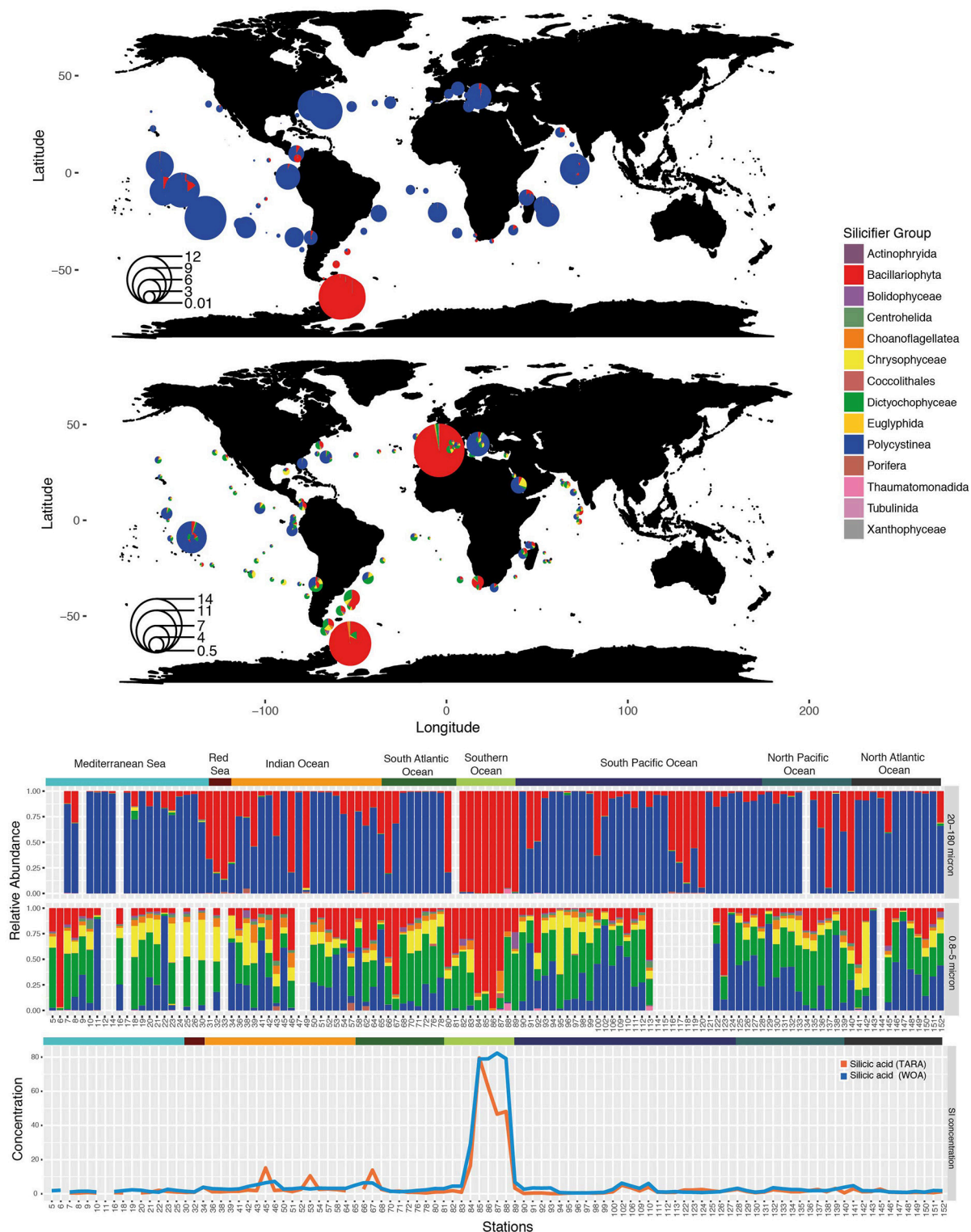


FIGURE 3 | Distribution of silicifiers in the sunlit ocean based on metabarcoding abundance data from the *Tara* Oceans expedition. **(Top)** Silicifiers in surface waters of the 20–180 micron size fraction—divide radius by 20 for log transformed relative abundance. **(Middle)** Silicifiers in surface waters of the 0.8–5 micron size fraction—divide radius by 30 for log transformed relative abundance. The size of the bubble corresponds to the importance of silicifiers with respect to the whole planktonic community. **(Bottom)** Composition of the silicifiers' community in surface waters at each sampling station and *in situ* silicic acid concentrations (in μM) obtained either from discrete *Tara* Oceans samples or from the World Ocean Atlas (woa13). Ocean provinces are indicated.

other, which may also reflect special adaptations to nutritional environments as opposed as eutrophic, oligotrophic, or HNLC areas.

Diatom expansion 65 Ma ago has been attributed to their superior competitive ability for silicic acid uptake relative to radiolarians, the latter experiencing a reduction in weight of their tests (Harper and Knoll, 1975). It is therefore expected that at high silicic acid concentrations, Radiolaria, with their inferior silicic acid uptake ability should have a better chance to thrive alongside diatoms. Yet, in the modern ocean, regions with high silicic acid concentrations (Southern Ocean, *Tara* stations TARA_084 to TARA_089) are still strongly dominated by large populations of diatoms (Platt et al., 2009) in which they can represent over three quarters of the whole planktonic community (Figure 3), according to the metabarcoding survey. This hints to the possibility that biotic or abiotic factors other than silicic uptake are responsible for diatom dominance.

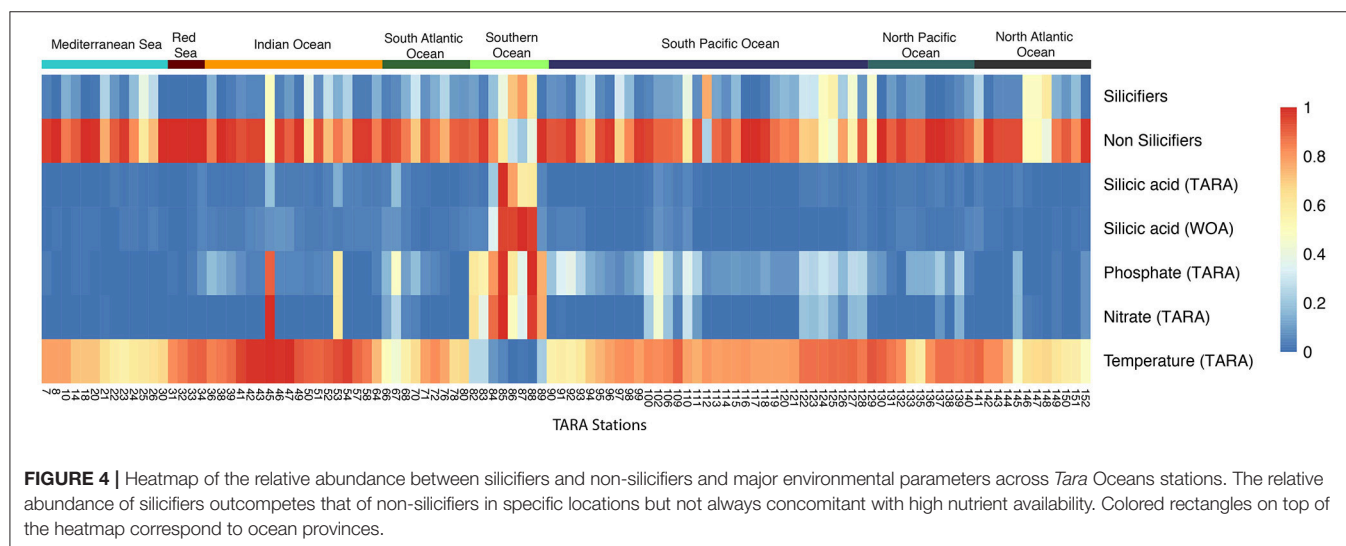
The relative abundance of the silica biomineralizing groups with respect to other micro-plankton in the *Tara* Oceans data (Figure 4) is largely dependent on nutrient availability (silicic acid, nitrate, phosphate), in particular in the Southern Ocean, the Indian Ocean and around the Marquesas Islands in the Pacific Ocean. However, silicic acid concentrations do not appear to be concomitant in specific stations in the Mediterranean Sea or in the North Atlantic Ocean where nutrient concentrations are low and yet silicifiers are highly abundant, perhaps reflecting a time lag between silicic acid availability and diatom uptake and bloom. Moreover, focused studies in the Mediterranean ecosystems do not report diatom dominance, with the exception of the spring bloom in the North West Mediterranean and Adriatic Sea. Most of the Mediterranean Sea is oligotrophic with diatoms restricted to more or less discrete deep layers at the boundary with the Levantine Intermediate Water (the saltiest water mass that forms in the eastern Mediterranean Sea), suggesting a strong bottom-up control by nutrients, including silicic acid (Leblanc et al., 2003; Crombet et al., 2011). Additionally, the North Atlantic planktonic community changes in the course of the productive season, and

silicic acid can also limit diatom uptake and growth (Leblanc et al., 2005).

Because some diatoms thrive in modestly nutrient-rich regions, other factors must therefore explain their success (Green et al., 2008). The continual reshaping of communities by mortality, allelopathy, symbiosis, and other processes show that community interactions exert strong selective pressure on marine microbes (Strom, 2008). This reflects the “Eltonian shortfall,” introduced by Hortal et al. (2015) in a review on current major flaws in biodiversity research and refers to our lack of knowledge about “biotic interactions.” It is likely that studying these top down pressures on biomineralizing organisms will complement our understanding of their evolution.

A prominent role of biomineralization in modern ecosystems is in defensive and feeding interactions between predators (feeding structures such as teeth) and prey (defensive structures such as spines, shells and tests). In embryophytes, silicification has a wide-ranging defensive role (He et al., 2014; Ensikat et al., 2016; Hartley et al., 2016), from abrasive phytoliths to complex structures such as trichomes, and even by inducing anti-herbivore and anti-pathogen metabolic responses (Ye et al., 2013). These defenses lead to multiple competitive interactions, with differential effects on different types of insect feeding (Massey et al., 2006), between insect and mammalian herbivores, or between large and small mammalian herbivores (Hartley et al., 2016). There are also complex competitive interactions between plants regarding their silicified defenses, which depend on various biotic (plant species, herbivore population cycles) and abiotic factors (soil conditions, climate; Garbuzov et al., 2011; Hartley et al., 2016). This can lead to herbivore-plant specialization and alter plant community and ecosystem structure.

Metazoan herbivores such as copepods (crustaceans) presumably exercise strong pressure on diatoms, silicoflagellates, and polycystines by feeding on them (Lebour, 1922; Marshall and Orr, 1955; Campbell et al., 2009; van Tol et al., 2012). Several feeding experiments have investigated the coevolution between



copepods and diatoms. Some adaptations are mechanical: copepods modify their feeding tools by increased silicification of the mouthparts (Itoh, 1970; Miller et al., 1980, 1990; Michels et al., 2012) in response to which diatoms adjust their protective frustules, leading to an arms race that fuels evolutionary processes (Hamm and Smetacek, 2007). Some diatoms that dominate blooms experience less grazing mortality than do co-occurring species (Assmy et al., 2007; Strom et al., 2007): it was shown that in the presence of preconditioned media that contained herbivores, diatoms develop grazing-resistant morphologies such as increased cell wall silicification (Pondaven et al., 2007; Ratti et al., 2013; Zhang et al., 2017). Silicification of diatom genera also depends on their ecological niche, wherein diatoms that thrive at depth under low light and in the nutrient gradient display low growth rates, and thus must be silicified to protect against grazing (Quéguiner, 2013). The silica cell wall therefore provides not only a “constitutive mechanical protection” for the cell but also a plastic trait that responds to grazing pressure promoting the diversification of ecological niches for a single taxonomic group. Differential biosilicification within a specific group may also have major effects on global nutrient recycling such as the decoupling of silicon and carbon cycles through complex biotic interactions influencing sedimentation pathways in the iron-limited Southern Ocean (e.g., Assmy et al., 2013; Quéguiner, 2013).

Experimental evidence suggests that biotic interactions not only shape the arms race between species, but also affect species range (Bateman et al., 2012; Araujo and Rozenfeld, 2014), inducing non-random co-distribution of species at large spatial scales of hundreds of kilometers for macro-organisms (Gotelli et al., 2010), both at regional and continental scales. Therefore, understanding the degree to which occurrences of species are constrained by the distributions of other species at broad scales of resolution and extent likely links back toward ecological and evolutionary mechanisms shaping the success of functional groups. This can be investigated through the use of co-occurrence networks (Gravel et al., 2011). Empirical studies have historically focused on competition (Gause, 1934; Hardin, 1960), revealing that in its extreme form competition leads to co-exclusion of the interacting species (MacArthur, 1972). As part of the recent *Tara* Oceans expedition, determinants of community structure in global ocean plankton communities were assessed using microbial association networks to create the *Tara* Oceans Interactome (Lima-Mendez et al., 2015). Pairwise links between species were computed based on how frequently they were found to co-occur in similar samples (positive correlations) or, on the contrary, if the presence of one organism negatively correlated with the presence of another (negative correlations). At a global scale (Figure 5), major taxonomic groups have shown higher positive correlations than negative ones, except diatoms and polycystines (Morueta-Holme et al., 2016). Instead diatoms and polycystines showed an unusually high proportion of negative correlations, which was statistically significant within silicifiers as a whole. This defines diatoms and polycystines as segregators. Conversely, plankton functional traits approaches show that silicifiers display a segregative pattern compared to other major interacting organisms in the plankton,

in particular toward meso- and proto-zooplankton as well as parasites (Figure 5). It is therefore the interplay between abiotic and biotic factors that shape the distribution of biomineralizing organisms in the modern ocean, in which competition for silicic acid coupled with differential grazing pressures seem to be important drivers of the spatio-temporal structure of silicifier communities across the ocean. The data in Figures 4, 5 indicate that temperature is a particularly important abiotic factor.

CELLULAR AND MOLECULAR ASPECTS OF EVOLUTIONARY COMPETITION

Evidence for evolutionary competition can also be found in the molecular biology of biomineralization. The gain, loss and convergence of the molecular mechanisms responsible for nutrient uptake and biomineral patterning illustrates how silicifying and non-silicifying organisms compete for common resources and produce similar solutions to solve these evolutionary problems.

Competition between diatom species has driven their diversification into various ecological niches (Sims et al., 2006; Nakov et al., 2014). This is mirrored in the diversification of diatom morphologies, from the macrostructural level of frustule shapes, spines and chains right down to the different micro- and nanopatterns of the frustule (Gordon et al., 2009; Finkel and Kotrc, 2010). Isolation of macromolecules found in diatom frustules, and *in vitro* studies of their silica polymerization activity, has led to the development of a model whereby micropatterns are produced by interactions between several components. Silica polymerizes on a structural scaffold composed of glycoproteins and other organic macromolecules, the ammonium fluoride insoluble matrix (Brunner et al., 2009; Tesson and Hildebrand, 2013; Kotzsch et al., 2016). The morphology and mesoscale patterning of the forming diatom silica is also controlled by interactions with the cytoskeleton as the silicon deposition vesicle (SDV) expands, and by components of the membrane surrounding the SDV (the silicalemma; Tesson and Hildebrand, 2010a,b; Tesson et al., 2017). The polymerization rate in these *in vitro* experiments, and therefore the nanoscale patterning (including formation of plates and pores), has been shown to be influenced by proteins including silaffins (Kröger et al., 2002), silacidins (Wenzl et al., 2008), and long-chain polyamines (LCPAs; Kröger et al., 2000; Sumper and Kröger, 2004). Some unique frustule structures are marked out by them containing specific biosilica-related proteins, such as cingulins that form the girdle bands linking the two valves of the frustule (Scheffel et al., 2011). The number, size and shape of girdle bands vary between diatom species, and this may be connected to variations in cingulin repertoires. Furthermore, it is not only the content and protein sequence of these molecules that has been demonstrated through *in vitro* experiments to control their silica polymerization and patterning activity, but also their ratios and post-translational processing like cleavage, glycosylation, phosphorylation, or the addition of quaternary ammonium groups (Kröger et al., 2002; Poulsen and Kröger, 2004; Lopez et al., 2005; Sumper et al., 2007; Wenzl et al., 2008).

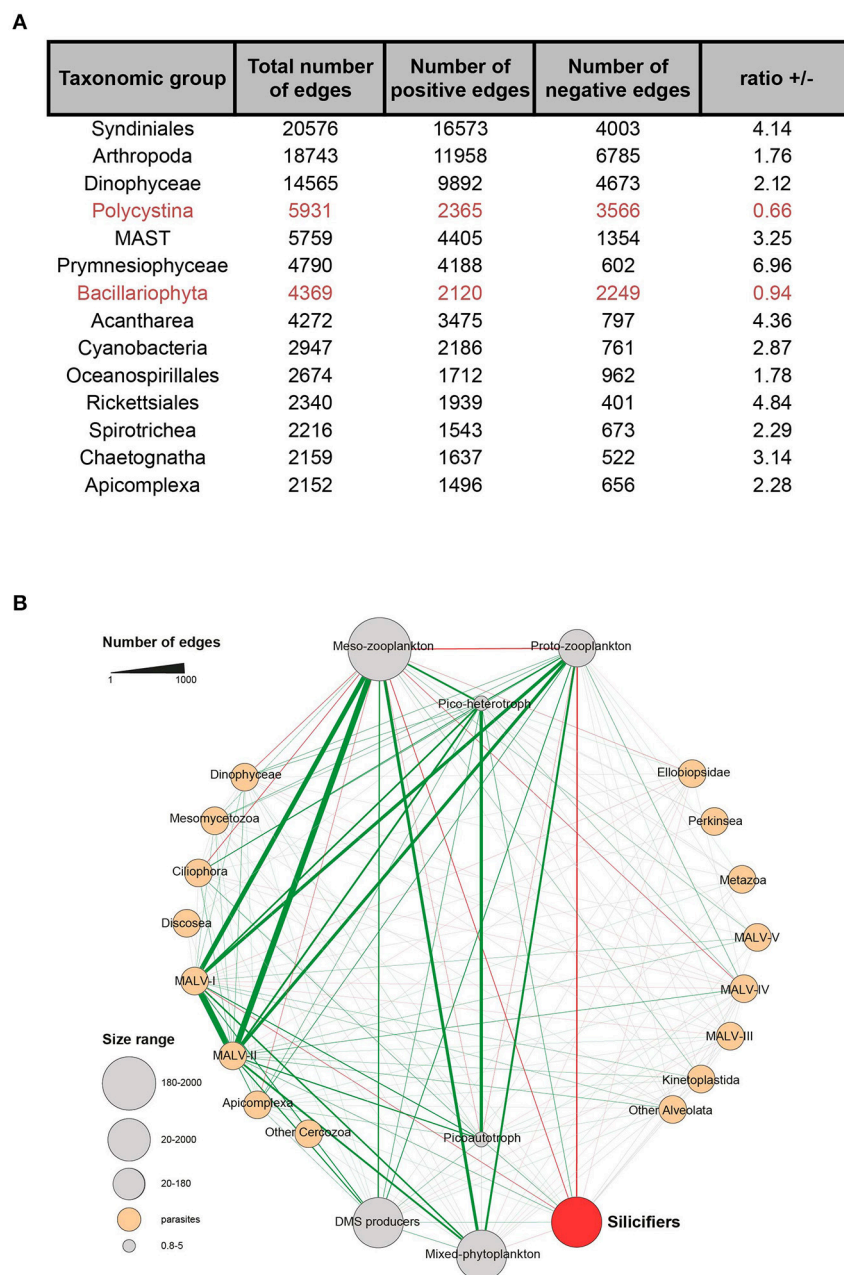


FIGURE 5 | Silicifiers in the Tara Oceans global ocean co-occurrence network. **(A)** Proportion of positive and negative correlations for the major taxonomic groups. Silicifiers are highlighted in red. **(B)** Plankton functional types (PFTs) subnetwork. PFTs encapsulate individual barcodes based on their trophic strategy and role in global biogeochemical cycles. Edges width reflects the number of correlations between the corresponding metanodes. Over-represented links (multiple-test corrected $P < 0.05$) are colored in green if they represent co-presences and in red if they represent exclusions; gray means non-overrepresented combinations. When both co-presences and exclusions were significant, the edge is shown as co-presence. Silicifiers encompass Bacillariophyta and Polycystina. Figure adapted from Lima-Mendez et al. (2015) and reproduced with permission from AAAS.

Diatom morphology can control features such as sinking rates (Smayda, 1970; Raven and Waite, 2004; Nakov et al., 2014), predation (Hamm et al., 2003; Pondaven et al., 2007), light perception (Fuhrmann et al., 2004; Yamanaka et al., 2008; Romann et al., 2015), viral resistance (Losic et al., 2006), and nutrient uptake (Finkel and Kotrc, 2010). Given that it has been

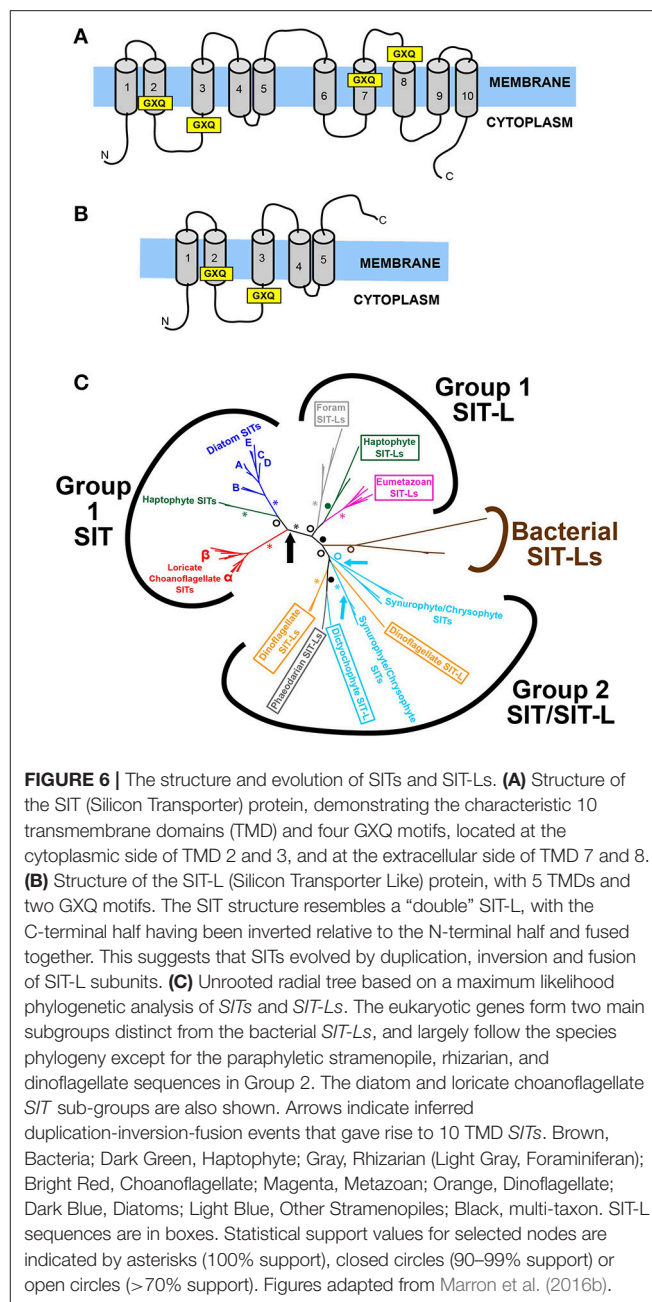
demonstrated that the content of the polymerization-influencing components differs between species (Kröger et al., 2000; Sumper and Lehmann, 2006; Bowler et al., 2008), it is conceivable that evolutionary modifications of the silica patterning mechanisms can help individuals to out-compete other diatoms in certain ecological niches. This would eventually lead to the emergence

of new species with characteristic morphologies of the siliceous frustule. In this way, the study of diatom silica formation and patterning mechanisms, combined with a phylogenetic framework, can reveal the evolutionary interactions between competition and frustule silicification.

In addition to diatoms, many other siliceous groups feature species-specific morphologies and micropatterning, with only limited variation depending on environmental conditions. Examples include loricate choanoflagellates (Leadbeater et al., 2009), thaumatomonads (Scoble and Cavalier-Smith, 2014), chrysophytes (van Tol et al., 2012), and ascidians (Monniot et al., 1992). Repeatedly we can observe the evolution of similar morphologies in distantly related taxa, such as micropores in the siliceous components of choanoflagellates (Leadbeater, 2015), chrysophytes (Sandgren et al., 1996), diatoms (Finkel and Kotrc, 2010), and haptophytes (Yoshida et al., 2006); spines and spicules in radiolarians (Kunitomo et al., 2006), dictyochophytes (Preisig, 1994), centrohelids (Zlatogursky, 2016), and sponges (Weaver et al., 2007); or tablets and scales in haptophytes (Yoshida et al., 2006), rhizarians (Nomura and Ishida, 2016), synurophytes (Sandgren et al., 1996), amoebozoans (Lahr et al., 2013), and brachiopods (Williams et al., 2001). Though the genes governing the production of these silica patterns are not fully understood, many parallels with the molecular biology of diatom silicification are emerging, such as a role for glycoproteins in choanoflagellates (Gong et al., 2010) and synurophytes (Ludwig et al., 1996), cytoskeleton-mediated shaping of the growing silica structure in multiple taxa (Leadbeater, 2015; Nomura and Ishida, 2016) and the presence of post-translationally modified LCPAs in haptophyte (Durak et al., 2016) and sponge (Matsunaga et al., 2007) silica. These polymerization mechanisms have apparently evolved independently from those in diatoms, suggesting repeated recruitment of similar molecules for silica formation and patterning, and therefore a similar role for silicification-related evolutionary competition and speciation as diatoms.

A critical step in silica biomineralization (Martin-Jézéquel et al., 2000), and therefore a major aspect of evolutionary competition between silicifiers, is the uptake and concentration of silicic acid from the external environment. The nature of this competition has changed over geological time in conjunction with changes in the biogeochemical cycling of silicon (Racki and Cordey, 2000; Maliva et al., 2005; Finkel and Kotrc, 2010; Knoll and Kotrc, 2015; Conley et al., 2017). In turn, this is reflected in the evolutionary molecular biology of silicon transport mechanisms.

The first proteins capable of transporting silicon across a plasma membrane to be identified were the SIT (Silicon Transporter) family (Hildebrand et al., 1997). The SIT protein (see **Figure 6A**) has a characteristic 10-transmembrane domain structure, with two conserved GXQ motifs arranged in a roughly symmetrical pattern at the cytoplasmic sides of transmembrane helices 2 and 3, and the extracellular sides of transmembrane helices 7 and 8 (Thamatrakoln et al., 2006). These motifs are proposed to be involved in forming an aqueous vestibule to allow an alternating access mechanism for silicon transport (in conjunction with Na⁺) across the membrane (Knight et al.,



2016). This four-GXQ domain characteristic of the *SIT* gene family is highly distinctive, being found only in the 10-transmembrane domain *SITs* and in the closely related, 5-transmembrane domain *SIT-Ls* (Silicon Transporter-Like; Durak et al., 2016). *SIT-Ls* resemble “halved-*SITs*” (see **Figure 6B**), and are believed to be the ancestral genes that underwent duplication to give rise to *SITs* (Durak et al., 2016; Marron et al., 2016b). This situation is analogous to the gene duplication and fusion events that are believed to have produced pseudo-symmetrical transporter proteins (Keller et al., 2014), exemplified best in the SWEET and semi-SWEET glucose transporters of eukaryotes and bacteria (Feng and Frommer, 2015; Tao et al., 2015).

Members of the Silicon Transporter gene family have been identified across a broad taxonomic range, in all eukaryotic supergroups save for archaeplastids, excavates and amoebozoans (with the caveat that no sequence data are currently available from silicifying excavates or amoebozoans) and are also found in some bacterial species. *SITs* are present in many highly-silicified species, most obviously siliceous stramenopiles (diatoms, chrysophyte/synurophytes, and dictyochophytes) but also siliceous choanoflagellates and haptophytes. In contrast *SIT-L* genes are often found in primarily calcareous groups (foraminifera, metazoans, calcareous haptophytes), although *SIT-Ls* were identified in silicifying groups such as phaeodarians and dinoflagellates. What is notable is that though some species contain multiple *SITs* or *SIT-Ls*, taxa expressing both *SIT* and *SIT-L* genes are rare: of the species examined only the haptophyte *Scyphosphaera apsteinii* possessed both, with the apparently non-silicifying dictyochophyte genus *Florenciella* having some evidence for both *SIT* and *SIT-L* genes (Marron et al., 2016b). This points to there being some sort of functional difference between *SIT* and *SIT-L* transporters, possibly with *SITs* being superior in some way, or with *SIT-L* genes being connected to calcification (Durak et al., 2016). It is notable that the geological record of heavily silicifying *SIT-L*-containing species show a decline in silicification and diversity (Lazarus et al., 2009; van Tol et al., 2012) coincident with the rise of the diatoms from the Mesozoic, again hinting at a “functional superiority” of *SITs* in competition for silicic acid uptake, though the nature of this advantage remains unresolved. Furthermore, siliceous sponges, which apparently lack either *SITs* or *SIT-Ls* (Marron et al., 2016b), show a similar decline in their degree of silicification and ecological dominance over this time (Maldonado et al., 1999). Again, this is suggestive of *SIT*-based mechanisms providing some type of competitive advantage over other uptake systems as silicic acid levels fell over geological time and competition for silicon increased.

When the *SIT/SIT-L* phylogeny is compared to species phylogenies, an interesting picture emerges (see **Figure 6C**). Three main eukaryotic clades are resolved: a monophyletic *SIT-only* clade containing diatom, choanoflagellate, and haptophyte genes; a monophyletic *SIT-L* only clade containing foraminiferan, metazoan, and haptophyte genes; and a polyphyletic clade featuring both *SIT* and *SIT-L* genes from radiolarians, dinoflagellates and various non-diatom stramenopiles (Marron et al., 2016b). In this analysis, the stramenopile *SITs* branch in two distinct groups with high statistical support, with diatoms being separate from chrysophytes/synurophytes, and dictyochophytes. This distinction also emerges when the phylogeny is analyzed with an alignment of *SIT-L*, *SIT* N-terminal and *SIT* C-terminal sequences (i.e., artificially splitting the *SITs* into two, roughly equal 5-transmembrane sequences each containing two GXQ motifs). In this case the diatom N- and C-termini branch with the relevant N- and C-termini of the choanoflagellate and haptophyte *SITs*. The 5-transmembrane sequences of other stramenopile *SITs* however branch paraphyletically, again together with radiolarian and dinoflagellate *SIT-Ls*. These phylogenies provide a strong molecular signal for the stramenopile *SITs* having evolved via multiple, independent duplications. In this scenario, the diatom

SITs arose from a single gene duplication and fusion event that also gave rise to the haptophyte and loricate choanoflagellate *SITs*, and must have occurred early in eukaryotic evolution, before these groups diverged deep in the Precambrian (Parfrey et al., 2011). The phylogenetic signal supports the scenario that the other stramenopile *SITs* arose from at least two other duplication-fusion events within the ochrophyte stramenopile clade itself, but after diatoms diverged, potentially as recently as the Mesozoic (Brown and Sorhannus, 2010; Derelle et al., 2016). It is hypothesized that this is a remarkable case of convergent molecular evolution, and that the independent invention of *SITs* from *SIT-Ls* was in response to competition for silicic acid from the rise of the diatoms after the Jurassic period (Marron et al., 2016b). As diatoms came to dominate the global silicon cycle, other heavily silicifying groups required more complex or more efficient uptake mechanisms and transporters to compete. What also emerges from these molecular analyses is that the last common ancestor of all ochrophytes must have possessed an *SIT-L* gene, and that diatoms have lost these *SIT-Ls*, again hinting at a superiority of *SITs* over *SIT-L*-based uptake systems in the competition for silicon.

Diatom domination of marine phytoplankton can be attributed to several ecological advantages (Armbrust et al., 2004), but of particular relevance to silicification is that they possess multiple modes of silicic acid uptake (Martin-Jézéquel et al., 2000; Thamtrakoln and Hildebrand, 2008). At lower silicic acid levels ($\leq 30 \mu\text{M}$), the majority of uptake is by *SIT*-mediated active transport, while at higher concentrations silicic acid enters the cell by diffusion (Thamtrakoln and Hildebrand, 2008; Shrestha and Hildebrand, 2015). The concentration gradient is created by binding of silicic acid to intracellular binding components in the cytoplasm, the character of which remains unknown (Thamtrakoln and Hildebrand, 2008; Spinde et al., 2011). This means that at higher silicic acid levels, diatoms can internally control uptake depending on the rate of silica polymerization in the SDV. The cytoplasmic binding compounds also allow diatoms to maintain a soluble intracellular silicon pool, with spare capacity permitting “surge uptake” of silicic acid following short-term silicon starvation (Thamtrakoln and Hildebrand, 2008). This is highly advantageous, allowing diatoms to take advantage of transient silicon sources in patchy environments like ocean gyres. The different modes of diatom silicic acid uptake are in contrast to other silicifiers such as sponges, which appear to only employ active transport and display maximum uptake efficiency at much higher silicic acid concentrations (Maldonado et al., 2011).

At ecologically-relevant silicon concentrations experienced by diatoms in modern oceans, active *SIT*-mediated uptake dominates. Diatom species generally possess multiple *SIT* genes (Hildebrand et al., 1998). These paralogs display differences in expression levels, the timing of their expression in the cell cycle, protein abundances and their sub-cellular localization (Thamtrakoln and Hildebrand, 2007; Sapriel et al., 2009; Shrestha et al., 2012; Shrestha and Hildebrand, 2015). These differences are believed to allow neofunctionalization of each *SIT*, evolving roles as silicon sensors, silicon transporters, targeting of different *SIT* proteins to specific cellular locations (Shrestha and

Hildebrand, 2015), specialization for the uptake of certain silicon species (Sapriel et al., 2009) or for differential characteristics of substrate affinity versus transport capacity. This allows for maximal uptake at various silicic acid concentrations in the external environment (Thamatrakoln et al., 2006; Thamatrakoln and Hildebrand, 2007, 2008). This suite of *SITs* is hypothesized to allow adaptation to varying conditions and allows the diatom cell to sense silicon availability, ensuring that it can meet the silicon requirements of frustule synthesis and so complete cell division.

This highlights the central role that silicon and silicification play in diatom biology (Martin-Jézéquel et al., 2000). Indeed, silicic acid limitation influences wider diatom cellular biology and results in transcriptional changes of genes related to multiple metabolic pathways (Mock et al., 2008; Shrestha et al., 2012), just as is seen for other essential nutrients like iron or nitrate. It is therefore unsurprising that diatoms have evolved such complex systems to accumulate and compete for silicic acid. This even extends to chemosensory responses of the motile raphid pennate diatom *Seminavis robusta* toward sources of silicic acid, and remarkably away from sources of germanium (Bondoc et al., 2016), since germanium exposure disrupts biosilicification and is therefore toxic to siliceous organisms (Marron et al., 2016a).

Phylogenetic evidence (see **Figure 6C**) demonstrates that *SIT* diversification occurred within the diatom lineage itself (Marron et al., 2016b). More detailed phylogenetic analyses of diatom *SITs* can be divided into five main clades (A–E), though the deep branching order between these clades is poorly resolved due to low statistical support (Durkin et al., 2016). The paraphyletic Clade B was found to be the most basal, and Clade B-type *SITs* are found throughout the various diatom groups. The other clades, however, have limited taxonomic distributions, for example Clade A only being present in pennate diatoms, and Clade E being unique to the Thalassiosirales. Therefore, diatom *SITs* underwent multiple independent duplications and diversifications within different lineages, with the more recently evolving diatom lineages (e.g., raphid pennates) having more complex *SIT* repertoires. This complexity is reflected in transcriptional analyses of diatoms under nutrient starvation, and in natural diatom assemblages. The expression levels and ratios of the various *SIT* clades differ according to silicic acid levels, with the more derived *SIT* types being more prominent over the basal Clade B *SITs* in low silicic acid environments compared to waters with higher silicic acid levels. This is hypothesized to allow diatom species to co-occur by employing different approaches to utilize limited silicic acid, and to out-compete other silicifying groups (Durkin et al., 2016). It also suggests a certain “directionality” of diatom *SIT* evolution, with new *SIT* clades evolving in new lineages to adapt to the drawdown of ocean silicic acid concentrations that occurred as the diatoms themselves diversified and came to dominate the oceans (Sims et al., 2006; Finkel and Kotrc, 2010).

Silicon Transporter diversification has also occurred in other taxa (see **Figure 6C**), with some stramenopiles expressing multiple *SITs*, and evidence for independent duplications of *SIT-Ls* in both foraminifera (*Ammonia* sp.) and Phaeodarian radiolarians (Marron et al., 2016b). The most prevalent case of this is in the siliceous loricated choanoflagellates, which display

evidence for a *SIT* gene duplication event early in their evolution (Leadbeater, 2015). All loricated choanoflagellates examined were found to possess two *SIT* gene types, termed *SIT α* and *SIT β* (Marron et al., 2016b). Transcriptional analysis of these *SIT* types under varying silicic acid concentrations demonstrated that the *SIT α* genes were highly expressed, and their expression levels responded to silicic acid availability, while the *SIT β* genes were always expressed at a low level, irrespective of the environmental silicic acid concentration. This closely resembles the situation in diatoms (see above), where some *SIT* genes are highly expressed and silicon-responsive, while other types have low expression unresponsive to silicon, suggesting that *SIT α* and *SIT β* have evolved different roles, possibly as specialized transporters or silicon sensors (Thamatrakoln and Hildebrand, 2007; Shrestha and Hildebrand, 2015). The similar diversification and sub-functionalization of *SITs* in parallel in both choanoflagellates and diatoms is proposed to be an example of convergent evolution in response to increased competition for silicic acid. This mirrors the hypothesis for the convergent evolution of 10-transmembrane domain *SITs* in the stramenopiles (see above). It is likely that future research will identify other cases of transporter diversification due to increased competition for silicic acid, potentially in the multiple rhizarian *SIT-Ls*, horsetail silicon transporters or the proposed silicon-related *Lsi2*-like gene family found in the siliceous sponges (Grégoire et al., 2012; Marron et al., 2016b; Vivancos et al., 2016).

The phylogenetic distribution of silicon-related active transporters reveals evidence for multiple and widespread losses of *SIT*, *SIT-L*, and *Lsi2*-like genes throughout the eukaryotes (Marron et al., 2016b). There is strong evidence for the loss of *SIT-Ls* across most bilaterian lineages, of losses of *SITs* and *SIT-Ls* across the coccolithophorid haptophytes and for losses of *SITs* and *SIT-Ls* multiple times throughout the stramenopiles. Indeed, barring rampant eukaryote-to-eukaryote horizontal gene transfer events (Ku et al., 2015), it is likely that *SITs* and/or *SIT-Ls* were present in the last common ancestor of all eukaryotes, and that multiple independent gene loss events only occurred after the main eukaryotic lineages and supergroups had diverged. Similarly, the distribution of *Lsi2*-like genes across the eukaryotes strongly supports that they were present in the eukaryotic last common ancestor (Marron et al., 2016b), but that they were independently lost in multiple lineages, for example deuterostome eumetazoans, fungi or apicomplexans.

It has been hypothesized that these active silicon transporters were originally required as part of a detoxification mechanism for life in the high-silicon Precambrian ocean (Marron et al., 2016b). Geological evidence for abiotic silica precipitation in sediments from the Neoproterozoic demonstrates that at the time that the eukaryote supergroups were originating and diversifying (Parfrey et al., 2011) oceanic silicic acid concentrations were high enough to allow autopolymerization into silica (Iler, 1979; Maliva et al., 1989, 2005; Siever, 1992; Grenne and Slack, 2003). Uncontrolled formation of silica free in the cytoplasm, potentially mediated by localized pH environments or accelerated by polyamines, would cause massive disruption to cellular metabolism. Unprotected by a membrane the freely polymerizing silica could occlude and adsorb proteins, nucleic acids, and other macromolecules

within its structure or on its surface (e.g., Betancor and Luckarift, 2008; Vandeventer et al., 2013). Therefore organisms must have required a system for silicon homeostasis, to bind or sequester silicic acid within the cytoplasm and then remove it from the cell. This is reflected in the bidirectional transportation capacity of SITs, where they could be employed to transport silicon out of the cell against a concentration gradient (Thamatrakoln and Hildebrand, 2008; Knight et al., 2016). In ancient oceans there would have been a strong selective pressure to maintain a molecular machinery for silicon detoxification, as has also been suggested for the employment of mucins as anti-calcification mechanisms in early animals (Marin et al., 1996; Wood et al., 2017).

Major geochemical and biological upheavals around the Precambrian/Cambrian boundary changed the competitive interactions and evolutionary pressures acting on these detoxification and homeostasis mechanisms. Most notable was the appearance and diversification of biomineralized hard parts (Knoll, 2003; Knoll and Kotrc, 2015), believed to have originated by modification and co-opting of the detoxification mechanisms (Wood et al., 2017). The innovation of biomineralized structures for feeding, movement and protection established an evolutionary arms race (Knoll, 2003; Cohen, 2005). This gave rise to biomineralization becoming more significant, with organisms producing larger and more prominent calcified or silicified structures. The biosilicified structures would have acted as silicon sinks, with the burial of biogenic silica skeletons sequestering silicon in the sediments. The outcome of this was that by the early Phanerozoic oceanic silicic acid concentrations were substantially reduced from Neoproterozoic levels (Maliva et al., 1989; Racki and Cordey, 2000), below the threshold for autopolymerization and removing the threat of harmful silica precipitation free in the cytoplasm. This would have removed the selective pressure to possess silicon detoxification mechanisms, and organisms could gain a competitive advantage by not diverting resources to such an unnecessary metabolic pathway, hence resulting in gene losses. The exception were those organisms which had re-deployed the silicon homeostasis machinery to produce siliceous structures. In these cases, silicon became a scarce resource, requiring the evolution of more sophisticated transport systems in the acquiring of silicic acid uptake to meet the metabolic requirements of biosilicification. This reflects the evolutionary biology of other elements, where they are initially toxic, before becoming metabolically useful and finally ending up as limiting nutrients and the subject of evolutionary competition (Rickaby, 2015).

In some cases, the solution to the problem of this scarcity was to secondarily lose biosilicification and the associated molecular mechanisms. An excellent example of this occurs within the haptophytes. Some species, such as *Prymnesium neolepis* (Yoshida et al., 2006) and *S. apsteinii* (Drescher et al., 2012) produce wholly- or partially siliceous scales, while some calcareous species such as *Calcidiscus leptoporus* possess SIT-Ls and have a metabolic requirement for silicon to complete normal production of their calcified scales (Durak et al., 2016). Other species however, have lost SIT-Ls (and SITs), and show no

effect of germanium toxicity disrupting biomineralization. One such species is *Emiliania huxleyi*, a calcifying haptophyte known to produce blooms of major ecological importance, and which is believed to have evolved relatively recently in the Cenozoic (Liu et al., 2010; Taylor et al., 2017). What is notable is that *E. huxleyi* blooms often occur following diatom blooms, raising the possibility that while diatoms enjoy a competitive advantage in silicon-replete waters, non-silicifying species like *E. huxleyi* have evolved to out-compete and succeed siliceous phytoplankton in silicon-deplete waters where they can continue to grow and produce biomineralized structures (Durak et al., 2016). In this way, the abandonment of any metabolic requirement for silicon opens new ecological niches and provides opportunities to gain new competitive advantages.

Molecular phylogenetics has revealed many other cases where non-silicifying species have evolved from heavily silicified ancestors. This is evident in land plants, with basal groups tending to be highly siliceous (e.g., liverworts) while some derived taxa (e.g., conifers) have low silicon contents and lack phytoliths (Hodson et al., 2005). Although there is some debate as to the evolutionary relationships between the main sponge groups (Sperling et al., 2010), the widespread distribution of non-siliceous species in otherwise siliceous sponge clades, and the similarity of the organic components of siliceous and collagenous skeletons, means that silicification was lost and/or re-evolved multiple times in the sponges (Ehrlich et al., 2007a,b; Maldonado, 2009; Kozhemyako et al., 2010). Similar evidence for independent losses and reinventions of biosilicification can be found in the centrohelids, a taxonomically enigmatic group of protists (Zlatogursky, 2016). Based on current phylogenetic data, centrohelids have evolved silicified structures ranging from scales to spines, but in some species these have been modified into organic-only scales and spines, or even been reduced so that the cell is covered only by a mucous sheath. Parallel evolution is also observed in the Arcellid testate amoebae, with convergent gains and losses of biosiliceous or organic tests (Lahr et al., 2013, 2015), or even the ability to form a test by agglutination of exogenous siliceous particles such as quartz grains, a strategy also developed by some coastal tintinnids.

A possible analog of the scenarios that saw these losses of biosilicification is the situation where silicification is facultative in some organisms (as opposed to the obligate silicification found in groups such as diatoms). This can occur under conditions of extreme silicon limitation, as in the tectiform choanoflagellates or synurophytes which produce naked, but otherwise healthy, cells if starved of silicon (Sandgren et al., 1996; Leadbeater, 2015). It may also be connected to stages in the life cycle, for example in juvenile brachiopods (Williams et al., 2001), or resembling in the haploid/diploid distinction between calcified and uncalcified stages of the *E. huxleyi* life cycle (Taylor et al., 2017) as has recently been suggested to occur in loricate choanoflagellates (Thomsen and Østergaard, 2017). The capacity for facultative silicification could be a combination of the two, as in the diatom *P. tricornutum*, unique amongst the diatoms in its ability to survive without a siliceous frustule. A combination of life cycle stage (Kessenich et al., 2014) and silicon availability (Yamada et al., 2014) has been put forward for explaining the evolution

of the naked bolidophytes and siliceous parmales. As these are the sister lineages to diatoms the molecular mechanisms regulating their biosilicification are crucial to understanding how the complex silicon-related metabolism of diatoms evolved.

We therefore observe how evolutionary competition and the associated trade-offs are central to the presence of silicification: biomineralized silica structures are only maintained when they confer a competitive advantage. Silicification would be lost when the total metabolic cost of biosilicification exceeds the benefit, for example due to the energetic cost of silicic acid acquisition or silica polymerization, restrictions on mobility due to the presence of a skeleton or the additional weight per unit volume of silica versus organic structures. Alternatively, it could be metabolically cheaper (either in cost of formation or of lifestyle trade-offs) to build a functionally equivalent structure from another biomineral (such as calcium phosphate or calcium carbonate shells), from organic components (e.g., chitin, cellulose, or collagen) or even to utilize the silica structures of other organisms (Lahr et al., 2015). Under this hypothesis these structures would provide similar competitive advantages, such as protection, while allowing survival in new (often silicon-depleted) niches. This could potentially lead to the loss of the molecular mechanisms for silicon transport and silica polymerization, producing a developmental legacy that restricts the potential for future evolutionary innovations, and reinforces the competitive interactions between silicifiers and non-silicifiers.

FUTURE DIRECTIONS

Recent years have witnessed several new discoveries that have expanded and improved our understanding of silica biomineralization. Fossil sampling and isotopic analyses of new sediment records have modified our view of the geological history of silicon biogeochemistry (Fontorbe et al., 2016). The massive increase in large-scale sequencing data has greatly aided research into the molecular biology of silica biomineralization, both through whole-genome sequencing within groups like diatoms and plants, and via transcriptome sequencing of new and previously poorly researched siliceous taxa (Keeling et al., 2014; Beisser et al., 2017; Caron et al., 2017; Tirichine et al., 2017). Many new genes associated with biosilicification have been identified (Kotzsch et al., 2016), including the recognition that active silicon transporter gene families are much more ancient and widely distributed amongst the eukaryotes than previously thought (Marron et al., 2016b). This has been complemented by the discovery of new silicifying species (Ichinomiya et al., 2011), most notably silicon accumulation in some strains of the hugely ecologically important cyanobacteria *Synechococcus* (Baines et al., 2012). Combined with metagenomic surveys and geochemical monitoring (Mutsaers et al., 2015; Sunagawa et al., 2015) it will be possible to gain a much deeper knowledge of the role of different marine groups in silicon biogeochemistry and how competitive interactions govern their ecology, distribution and response to changing climatic conditions (Mock et al., 2016).

These advances have contributed to hypotheses for a greater role of silicon in biology, for example in protein folding (Eglin et al., 2006). We are also beginning to recognize a link between phosphate transporters and silicic acid uptake in groups as disparate as cyanobacteria and mammals (Brzezinski et al., 2017; Ratcliffe et al., 2017) that may be underpinned by a more general system for metalloid metabolism (Bienert et al., 2007). This could contribute to satisfying metabolic requirements for silicon in taxa like phaeophyte brown algae, which are known to biosilicify (Mizuta and Yasui, 2012; Tarakhovskaya et al., 2012) but with no currently identified silicon transporter genes (Marron et al., 2016b). These observations blur the boundary between silicifying and non-silicifying species, illustrated by the requirement for silicon in processes such as haptophyte calcium carbonate formation (Durak et al., 2016), amorphous calcium carbonate formation in plant cystoliths (Gal et al., 2012) and in the early developmental stages of the vertebrate calcium phosphate skeleton (Carlisle, 1981); or given the uptake of silicic acid (Fuhrman et al., 1978) and presence of silicon transporters in apparently non-mineralizing species (e.g., *Florenciella*; Marron et al., 2016b). This has implications for understanding the evolution and competitive interactions between silicifiers and non-silicifiers in the living world.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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